

REMARKS

This paper is being provided in response to the November 5, 2002 Office Action for the above-referenced application. In this response, applicant has amended claims 1, 8, and 30 in order to clarify that which Applicant deems to be the invention. Applicant respectfully submits that the amendments to the claims are all supported by the originally filed application.

The rejection of claims 1-11 and 13-36 under 35 U.S.C. §103(a) as being obvious over U.S. Patent No. 6,146,959 (hereinafter referred to as “DeBoer”) or U.S. Patent No. 6,057,189 (hereinafter referred to as “Huang”) in view of U.S. Patent No. 6,087,261 (hereinafter referred to as “Nishikawa”) or U.S. Patent No. 6,103,566 (hereinafter referred to as “Tamaru”) or U.S. Patent No. 6,010,940 (hereinafter referred to as “Lee”) is hereby traversed and reconsideration thereof is respectfully requested. Applicant respectfully submits that the claims, as amended herein, are patentable over the cited references, whether taken separately or in any combination.

Claim 1 recites a method for forming a semiconductor device having a laminated structure including a dielectric film made from a metal oxide formed on a surface of a heated substrate and a CVD high melting point metal nitride film, where the metal nitride film is directly formed on said dielectric film by introducing a source gas containing the high melting point metal into a chamber in which the substrate is contained, the method including a step of heating the substrate in an ambient that is non-reactive with respect to the metal oxide formed on the surface of the substrate in the chamber (*i.e.*, an ambient

that has no components that react with the metal oxide) where the non-reactive ambient includes at least one of a gas non-reactive with respect to the metal oxide contained in the dielectric film and NH₃ gas, and introducing into the chamber a source gas for forming the CVD-TiN film and NH₃ gas, following the heating step, and further where a temperature of the substrate is set at a prescribed temperature, before the source gas containing the high melting point metal is introduced into the chamber.

Claims 2 through 7 depend from claim 1 and recite further patentable features over the base claim. Dependent claim 2 recites that the non-reactive ambient treating step has a flow stabilizing step. Dependent claim 3 recites that the non-reactive gas is introduced during the flow stabilizing step. Dependent claim 4 recites that the treating step heats the substrate and the flow stabilizing step is after the heating step. Dependent claim 5 recites that the NH₃ gas is introduced into the chamber during the heating step. Dependent claim 6 recites that the NH₃ gas has a NH₃ partial pressure of no greater than 1.0 Torr and no less than 0.1 Torr. Dependent claim 7 recites that the non-reactive gas and the NH₃ gas are introduced into the chamber during flow stabilizing step.

Claim 8 recites a method for forming a semiconductor device having a laminated structure of a dielectric made from a metal oxide and a CVD high melting point metal nitride film. The metal nitride film is directly formed on the dielectric film by a source gas containing the high melting point metal in a chamber in which the dielectric is contained. The method heats a substrate to a prescribed temperature in an ambient with an NH₃ partial pressure no greater than 1.0 Torr and no less than 0.1 Torr before the

introduction of the source gas containing the high melting point metal. The NH₃ gas does not react with the dielectric film.

Claims 9-10 depend from claim 8 and recite further patentable features over the base claim. Dependent claim 9 recites a step of heating the substrate to a prescribed temperature and maintaining the temperature in a non-reactive gas, which is neither oxidizing nor reducing with respect to the metal oxide, and while the gas flow is stabilized. Dependent claim 10 recites that the NH₃ gas is introduced during the second half of the CVD film growing step.

Claims 11 and 13-29 depend from claim 1 and recite further patentable features over the base claim. Dependent claim 11 recites a step that is performed before the CVD high melting point metal nitride film is formed, of heating the substrate (on which the dielectric film made from a metal oxide is formed) in the chamber while introducing the non-reactive gas. Then performing a step of forming the high melting point metal nitride film on the dielectric film by introducing a gas mixture comprising the NH₃ gas and the non-reactive gas, the non-reactive gas being in a volume amount that is larger than the NH₃ gas, and the source gas amount having less volume than the NH₃ gas. Dependent claim 13, as amended herein, recites that the dielectric film is a tantalum oxide (Ta₂O₅) film. Dependent claim 14 recites that the substrate is heated to between approximately 400°C and 700°C before the source gas containing the high melting point metal is introduced. Dependent claim 15 recites that the non-reactive gas is selected from a list of nitrogen, argon, hydrogen gas, or a mixture of these gases. Dependent claim 16 recites

that the high melting point metal nitride film is a TiN film. Dependent claim 17 recites that the source gas containing titanium is selected from the group consisting of titanium tetrachloride ($TiCl_4$), tetrakis dimethyl amino titanium (TDMAT), tetrakis diethyl amino titanium (TDEAT). Dependent claim 18 recites that the high melting point metal nitride film is alternately a WN film, and WF_6 gas is introduced as a source gas. Dependent claim 19 recites that the device has a capacitive element, a dielectric film, a CVD high melting point metal nitride film as a protective film between the dielectric film and the capacitive element. Dependent claim 20 recites that the device has a MOSFET where the CVD high melting point metal nitride layer is the lowermost layer of the laminated gate electrode layer. Dependent claim 21 recites raising the partial pressure of the NH_3 gas during a second half of forming the CVD film on the metal oxide, so that annealing is done by the NH_3 gas. Dependent claim 22 recites that the dielectric film is a tantalum oxide (Ta_2O_5) film. Dependent claim 23 recites that the substrate is heated between approximately 400°C and 700°C. Dependent claim 24 recites that the non-reactive gas is selected from nitrogen, argon, hydrogen gas, or a mixture of these gases. Dependent claim 25 recites the high melting point metal nitride film is TiN. Dependent claim 26 recites the source gas containing titanium is selected from the group consisting of titanium tetrachloride ($TiCl_4$), tetrakis dimethyl amino titanium (TDMAT), tetrakis diethyl amino titanium (TDEAT). Dependent claim 27 recites that the high melting point metal nitride film is a WN film, and WF_6 gas is introduced as a source gas containing tungsten. Dependent claim 28 recites that the semiconductor device has a capacitive element, a dielectric film, and a CVD high melting point metal nitride film as a protective film between the dielectric film and capacitive element. Dependent claim 29 recites that

the semiconductor device has a MOSFET with a gate insulation film and the CVD high melting point metal nitride layer is the lowermost layer of the laminated gate electrode layer formed on the gate insulation film.

Independent claim 30 recites a method for forming a CVD-TiN film, wherein a titanium nitride (TiN) film is formed on a dielectric film that includes an oxide material formed by a CVD film forming process within a CVD film forming device. The method includes heating a substrate with the dielectric film in the CVD film forming device in an atmosphere that is non-reactive with respect to the dielectric film, including the oxide. Then forming the titanium nitride (TiN) film on the dielectric film in the CVD film forming device.

Claims 31 to 36 depend from independent claim 30, and recited further patentable features over the base claim. Claim 31 recites that the dielectric film including said oxide material is a tantalum oxide (Ta_2O_5) film. Claim 32 recites that the substrate is heated to a temperature of approximately 400°C to no greater than approximately 700°C. Claim 33 recites that the atmosphere including the non-reactive gas with the tantalum oxide comprises gases other than the NH_3 gas. Claim 34 recites that the atmosphere of non-reactive gas with the tantalum oxide comprises one gas selected from a rarified gas including nitrogen, argon, hydrogen gas, or a mixture of these gases. Claim 35 recites that the non-reactive gas is a mixture of titanium tetrachloride ($TiCl_4$) and NH_3 . Claim 36 recites that the tantalum oxide film is formed as a capacitive film of a capacitor element and the CVD-TiN film is formed as a plate electrode.

DeBoer discloses a method of forming capacitors containing the metal tantalum. The disclosed method forms a dielectric layer having a dielectric constant of about 25 for a capacitor on a metal layer, typically hemispherical polycrystalline silicon. A silicon nitride layer 36 is deposited over the poly capacitor plate 34 in order to prevent the tantalum oxide layer from interacting negatively with the polysilicon layer 34. A first tantalum oxide layer 38 is formed over the nitride layer 36 and then a second tantalum layer 40 is formed by heating the first tantalum layer in an ambient containing nitrogen, such as ammonia. The tantalum layer 40 is thus tantalum nitride or tantalum oxynitride. Another metal nitride layer 42, such as titanium nitride or tungsten nitride, is formed over the second tantalum layer to provide protection for the tantalum oxide from the second polysilicon capacitor plate 44 (see col. 5, line 5).

Huang discloses a method of fabricating a capacitor using ion implantation to form a barrier layer of the outer part of the hemispherical poly silicon capacitor plate. The polysilicon is ion implanted with nitrogen ions at 30 KeV to form a silicon nitride barrier layer to protect the future tantalum oxide dielectric from the polysilicon. The tantalum oxide is CVD deposited on the barrier layer, and then densified by annealing in oxygen or nitrogen (col. 4, line 54), to improve the electrical characteristics of the dielectric.

Nishikawa discloses a method of forming a dielectric film on a semiconductor substrate in a reduced pressure atmosphere, and then depositing a metal or metal nitride

on the dielectric. Nishikawa discloses that hydrogen, carbon and methane released as a normal part of the CVD deposition causes electrical leakage in the dielectric film. Nishikawa discloses that this electrical leakage problem is reduced by using oxygen containing gases in the formation of the conductor film (col. 2, lines 18-27; col. 4, line 66; col. 9, line 15). Nishikawa states that this step is extremely important (col. 2, line 63). The Nishikawa reference discloses that using a reaction gas that contains oxygen at up to 5 sccm (col. 5, line 23) produces an oxygen containing metal film that does not have too high a resistivity to be a useful conductor. The oxidizing gas may be selected from oxygen, peroxide, water, ozone, carbon monoxide, carbon dioxide, nitrous oxide etc (col. 5, line 35 and col. 14, line 47) with the amount kept low through the middle stage of the formation of the conductor (col. 3, line 12) to keep the metal resistance high enough to be a good conductor (col. 4, line 60 and Fig 2).

Tamaru discloses a DRAM with a capacitive element that is protected from breakdown under the influence of a TiN film that is CVD deposited on the capacitor dielectric by a passivation film, thus preventing the dielectric from making any contact with the nitrogen containing reducing gas (col. 3, lines 25 and 49). The Tamaru reference discloses the use of ammonia to passivate the polysilicon lower electrode (col. 2, lines 10-24), but contains no suggestion of any ammonia or reducing gas used after the dielectric is formed (col. 3, lines 30 and 49; col. 4, line 20) until after a oxygen containing titanium source gas has covered the metal oxide (col. 18, lines 33- 40). The Tamaru reference discloses that the metal oxide should not come into contact with reducing gases such as ammonia.

Lee discloses a method for making a TiN barrier for a capacitor upper plate to reduce the reactions between the metal oxide and the polysilicon upper electrode (col. 1, line 26). The TiN layer is disclosed as being formed using $TiCl_4$, which may form a material that may attack the metal oxide. This chlorine may be reduced by use of an ammonia anneal which chemically attacks the chlorine and removes it as HCl gas. The anneal step is disclosed as occurring after the TiN deposition.

Applicant respectfully submits that neither Nishikawa, nor Tamaru, nor Lee disclose CVD of a metal nitride layer onto a metal oxide layer in a non-reactive ambient, as required by all pending claims. Nishikawa discloses the use of oxidizing gases to avoid electrical leakage (col. 2, lines 18-27; col. 4, line 66; col. 9, line 15), and states that this step is extremely important (col. 2, line 63). Tamaru discloses the use of ammonia to passivate a surface (col. 2, lines 10-24), and cautions that the metal oxide should not come into contact with reducing gases such as ammonia. Lee uses $TiCl_4$ to form the TiN layer, and cautions that this gas may form chlorine, which attacks the metal oxide (col. 3, lines 39-44). This chlorine is reduced by the use of an ammonia anneal subsequent to the formation of the TiN layer, so that the metal oxide layer is not exposed to the ammonia gas (col. 6, lines 34-36). Thus, in each case, the ambient contains a reactive gas (as a concentration sufficiently large that the reactive component actually reacts with the metal oxide layer), in addition to any non-reactive gases that may be present. Independent claims 1, 8, and 30 have been amended with this response to clarify that the entire

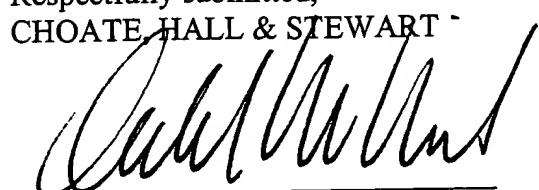
ambient is non-reactive; *i.e.*, that no component of the ambient reacts with the metal oxide layer.

Furthermore, neither DeBoer nor Huang can remedy these failings of Nishikawa, Tamaru, and Lee. DeBoer teaches growing a nitride film from reactive conversion of a tantalum oxide layer, which obviously requires a reaction with that oxide layer, and further does not even use a CVD process. Huang forms a TiN film by sputtering atop a tantalum oxide layer. Sputtering must occur in vacuum, and therefore cannot occur under a non-reactive ambient as recited by the pending claims. Thus, neither reference uses a CVD process to form the nitride film, and neither can properly be said to teach or suggest the completely non-reactive ambient for CVD of the present invention.

Applicant further submits that DeBoer and Huang constitute nonanalogous art that may not even properly be used in a rejection under 35 U.S.C. 103(a) of the present invention. The present invention relates to chemical vapor deposition of a metal nitride film. Applicant submits that one of ordinary skill in the art would not normally look at methods of deposition outside of CVD when determining how to minimize the adverse effects of performing CVD. Thus, even if DeBoer and Huang taught a non-reactive anneal according to the present invention (which they do NOT), they could not properly be combined with the other cited references in order to make out a *prima facie* rejection under 35 U.S.C. 103(a).

Based on the above, applicant respectfully requests that the Examiner reconsider and withdraw all outstanding rejections and objections. Favorable consideration and allowance are earnestly solicited. Should there be any questions after reviewing this paper, the Examiner is invited to contact the undersigned at 617-248-4038.

Respectfully submitted,
CHOATE HALL & STEWART


Donald W. Muirhead
Registration No. 33,978

Date: February 3, 2003

Patent Group
Choate, Hall & Stewart
53 State Street
Boston, MA 02109

Clean copy of amendments made herein

1. (Five Times Amended) A method for forming a semiconductor device having a laminated structure including a dielectric film made from a metal oxide formed on a surface of a heated substrate and a CVD high melting point metal nitride film, wherein said metal nitride film is directly formed on said dielectric film by introducing a source gas containing said high melting point metal into a chamber in which said substrate is contained,

said method comprising a step of heating said substrate in a non-reactive ambient having no component that reacts with said metal oxide formed on said surface of said substrate in said chamber, wherein said non-reactive ambient includes a member of the group consisting of a gas non-reactive with respect to said metal oxide contained in said dielectric film and NH₃ gas, and

introducing into said chamber a source gas for forming said CVD-TiN film and NH₃ gas, following said heating step, and further

wherein a temperature of said substrate is set at a prescribed temperature, before said source gas containing said high melting point metal is introduced into said chamber.

8. (Four Times Amended) A method for forming a semiconductor device having a laminated structure of a dielectric made from a metal oxide and a CVD high melting point metal nitride film formed thereover, wherein said metal nitride film is directly formed on said dielectric film by introducing a source gas containing said high melting point metal into a chamber in which said dielectric film is contained, said method comprising;

heating a substrate onto which said dielectric film is formed to a prescribed

temperature in an ambient comprising NH₃ gas at a partial pressure no greater than 1.0 Torr and no less than 0.1 Torr before the introduction of said source gas containing said high melting point metal, wherein said NH₃ gas does not react with said dielectric film.

30. (Once Amended) A method for forming a CVD-TiN film, wherein a titanium nitride (TiN) film is formed on a dielectric film that includes an oxide material formed by a CVD film forming process within a CVD film forming device, said method comprising:
heating a substrate provided with said dielectric film in said CVD film forming device, within an atmosphere having no component which reacts with said dielectric film including said oxide material; and
forming said titanium nitride (TiN) film on said dielectric film in said CVD film forming device.